PHASE TRANSITIONS IN POLYMER BLENDS AND BLOCK COPOLYMERS INDUCED BY SELECTIVE DILATION WITH SUPERCRITICAL CO$_2$

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1. Introduction

Supercritical fluids (SCFs) offer a number of advantages for the synthesis and processing of polymeric materials. Early work in the field focused on the high-pressure polymerization of ethylene or exploited the adjustable physicochemical properties of SCFs, including density and dielectric constant, for the fractionation, extraction and impregnation of polymers.[1] Recently, the field has expanded to include polymer synthesis and modification by reactive processing in the presence of CO$_2$. With few exceptions these are heterogeneous processes that are facilitated by enhanced transport within the SCF-swollen polymer and are sensitive to the partitioning of solutes between the fluid and polymer phases. Examples include heterogeneous dispersion polymerizations in CO$_2$[2], condensation reactions in dilated melts[3], and the preparation of composite materials by conducting chemical reactions directly within solid polymers swollen by CO$_2$.[4]

In binary CO$_2$/polymer systems, sorption of the fluid within the polymer is well understood and has been successfully modeled using lattice-fluid theory.[5,6] In these systems, the sorbed fluid primarily plays the role of a reversible plasticizing agent that can severely depress the glass transition temperature[7], reduce viscosity[8] and increase molecular mobility (diffusivities) within the polymer matrix.[9,10] The degree of sorption, and thus the magnitude of the effect on transport properties, can be controlled by pressure mediated adjustments in CO$_2$ density. For example, in this volume Gulari reports CO$_2$-induced reductions in viscosity for polystyrene/CO$_2$ and polydimethylsiloxane/CO$_2$ binaries that are in line with free volume predictions.[8] Other groups have demonstrated CO$_2$-mediated enhancements in penetrant diffusion coefficients within SCF/polymer binaries of up to six orders of magnitude.[9,10]

A natural evolution of past work is to extend the benefits of processing in CO$_2$ to multi-component polymer systems. Potential applications include the modification and orientation of block copolymers, the preparation of homogeneous blends, and improving the efficiency of melt-phase blend compatibilization reactions. In this chapter, we show that for these systems, CO$_2$ sorption not only influences molecular mobility, but can also have a dramatic effect on polymer/polymer compatibility that can

not be predicted based on the behavior of liquid solvents or hydrostatic pressure. Specifically, we find that dilation of symmetric d-polystyrene-b-poly(n-butyl methacrylate) block copolymer melts and two binary blends, deuterated polystyrene/poly(vinyl methyl ether), denoted d-PS/PVME, and deuterated polystyrene/poly(n-butyl methacrylate), denoted d-PS/PnBMA, with CO_2 can induce lower critical transitions at temperatures hundreds of degrees below those at ambient pressure.[11] Moreover the location of these sorption-induced transition temperatures can be precisely tuned by controlling the degree of CO_2 uptake via pressure-mediated adjustments in CO_2 density over broad ranges. The appearance of solvent-induced segregation in blends may be undesirable, but such phase behavior in block copolymers is advantageous. Sorption of CO_2 drives the system to stronger states of segregation while simultaneously enhancing diffusion and reducing viscosity relative to the segregated melt. This unique combination of attributes provides new opportunities for processing, orienting and chemically modifying segregated copolymers to yield advanced, structured materials and composites.

2.   Polymer Phase Behavior

2.1 POLYMER BLENDS AND BLOCK COPOLYMERS

Mixing of large molecular chains provides only a small entropy gain and thus miscibility in homopolymer blends and block copolymers is governed by a delicate balance between enthalpic and non-combinatorial entropic contributions to the energy of segmental interactions. These interactions are described by the well known temperature and composition dependent Flory-Huggins parameter, χ.[12] Phase separation occurs, upon either heating or cooling from the homogeneous melt when the product of χ and the number of polymer segments, N exceeds a critical value of 2.0 for blends and 10.5 for symmetric copolymers (Figure 1).[13] It has long been appreciated that the low temperature stability limit, called the upper critical solution temperature (UCST) for polymer blends or upper order-disorder temperature (UODT) for block copolymers, is dictated by enthalpic factors: demixing occurs when sufficient thermal energy is no longer available to overcome repulsive interactions between unlike segments. The nature of the high stability limit, called the lower critical solution temperature (LCST) in polymer blends or the lower disorder-order transition (LDOT) in block copolymers[15] is more subtle. A straightforward stability analysis indicates that entropy changes must be positive upon segregation.[14] The requisite increase in χ that drives the transition can be attributed to enthalpic or entropic factors, acting alone or in combination. In systems with strong specific interactions between segments, the favorable enthalpic contribution to miscibility weakens until it can no longer overcome the entropic penalty associated with maintaining contact-mediated, preferred orientations between the interacting segments. In the absence of strong interactions between segments, phase separation is driven by negative volume changes upon mixing that arise due to the widening disparities between the free volumes of the phases as temperature increases. This "equation of state effect" reflects differences in compressibilities between the mixture components and can be drawn directly by differentiation of the Gibbs free energy of mixing.[14]

Polymer phase transitions are traditionally probed by exploiting the temperature dependence of χ to induce segregation. The location of the transition can be readily changed by adjusting the component volume fractions, ϕ or N. Recently the effects of liquid organic solvents[16,17], homopolymer diluents[18] and pressure[19-25] have been studied in efforts to assess the phase behavior of blends and copolymers under realistic processing conditions.
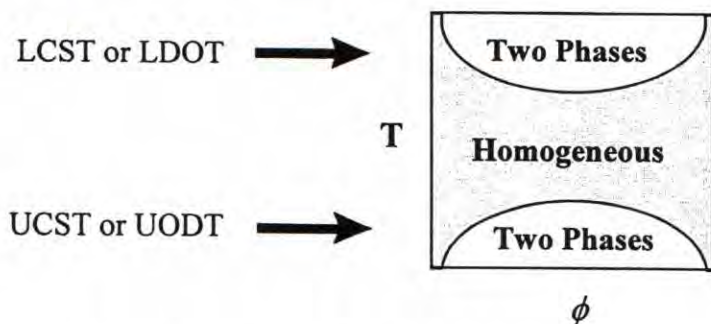

Figure 1. Schematic diagram of polymer blend and diblock copolymer phase behavior for systems that exhibit a miscibility gap.

2.2 LCSTs IN POLYMER SOLUTIONS AND THE INFLUENCE OF COMPRESSIBLE DILUENTS

Unlike polymer mixtures, the origin of lower critical solution transitions in most polymer solutions is unambiguous. Phase separation occurs at temperatures between 0.7 and 0.9 T_c, where T_c is the critical temperature of the light component, due to widening disparities between the free volumes of the polymer and solvent as temperature increases.[14] This simple heuristic is quite general and can be applied to multi-component solvents, including those that contain a compressible diluent. For example, McHugh and Guckes demonstrated that the LCSTs of an ethylene-propylene (E-P) copolymer in a mixed liquid hydrocarbon solvent could be depressed by as much as 100 °C upon the addition of compressible diluents including ethylene, propylene and CO_2.[26] McClellan and McHugh subsequently showed that the LCSTs in the E-P copolymer/hexane system could be systematically depressed upon the addition of ethane until they merged with the UCST, causing immiscibility at all conditions.[27] These results indicate that dilation of a light component with a high free-volume supercritical fluid diluent, which increases the compressibility of the solvent, can dramatically shift the location of the LCST in polymer solutions. Kiran reported a transition from LCST to UCST behavior in the ternary polyethylene, pentane, carbon dioxide system as the loading of CO_2 was increased.[28] An extensive discussion of this work is provided in another chapter in this volume.

2.3 BINARY HOMOPOLYMER/SCF SYSTEMS

Numerous studies of SCF sorption in polymers have been conducted.[29] Carbon dioxide is a poor solvent for most polymers (exceptions include siloxanes and amorphous fluoropolymers), but gas permeability data suggest virtually all polymers can be swollen by it.[30] Figure 2a shows the solubility of CO_2 in polystyrene and poly(n-butyl methacrylate).[31,32] Pressure mediated adjustments in solvent density provide a convenient lever by which the degree of sorption can be controlled. Lattice-fluid models including the Sanchez-Lacombe (S-L) and Panayiotou-Vera equations of state faithfully reproduce both mass uptake and volumetric dilation using a single adjustable parameter, provided the pure-component parameters are correlated over the experimental range of interest.[7] Little data is available for CO_2 sorption in blends. An exception is the work of Monnerie and colleagues who studied sorption and diffusion in PS/PVME blends of various compositions (Figure 2b).[33] The solid curves overlain on the literature data in Figures 2a and 2b were generated using the S-L equation (see section 4.1). Once accurate sorption curves are obtained, the equations can be used to calculate derived properties such as isothermal compressibility, κ. As we shall see, these calculations provide insight into the nature of the SCF-induced transitions.
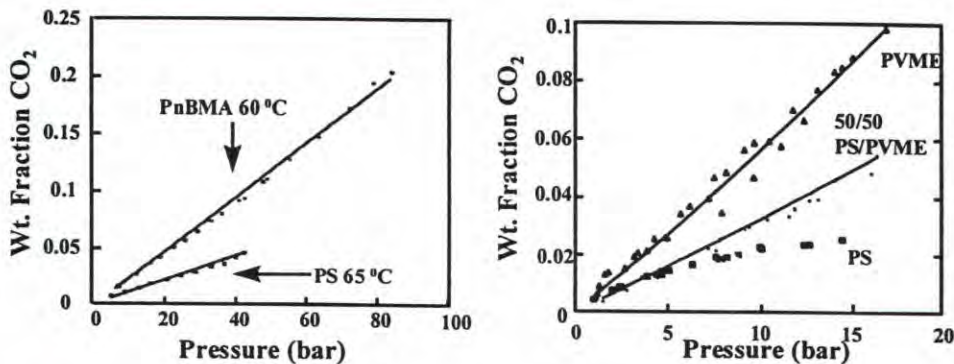

Figure 2. a.) CO_2 sorption in polystyrene and poly(n-butyl methacrylate). The solid lines are calculated results using the Sanchez-Lacombe equation of state with binary interaction parameters, δ_{ij} of 0.05 and –0.004 for PS/CO_2 and $PnBMA/CO_2$ respectively. b.) CO_2 sorption in PS, PVME and a PS/PVME blend at 20.6 $^{\circ}$C. Solid lines are S-L fits using a δ_{ij} of –0.04 for $PVME/CO_2$ and 0.018 for the pseudo-binary blend/CO_2 system (see section 4 for details).

3. Experimental

The phase behavior of symmetric P(d-S-b-nBMA) copolymer melts and two binary blends, d-PS/PnBMA and d-PS/PVME, in the presence of compressed carbon dioxide was studied *in situ* using small angle neutron scattering. The block copolymers were synthesized by standard living anionic polymerization: n-butyl lithium was added to

deuterated styrene in cylohexane. Sequential addition of n-butyl methacrylate yielded P(d-S-b-nBMA). Symmetric, diblock P(d-S-b-nBMA) copolymers having total molecular weights of 32,000 and 78,000 g/mol, denoted 32K and 78K, respectively, were melt pressed at 120 ^{0}C into 1.3 cm (o.d.) by 2.5 mm thick disks that were inserted into stainless-steel sample rings. Blends of 40% d-PS and 60% PnBMA having molecular weights 14,000 and 15,000 g/mol respectively were cast from toluene, dried and melt pressed directly into the sample rings at 60 ^{0}C. Blends of d-PS and PVME having molecular weights 90,000 and 104,000 g/mol, respectively, were prepared in the same manner. Scattering profiles were collected as a function of CO_2 density at temperatures between ambient and 200 ^{0}C and pressures between atmospheric and 350 bar in a stainless steel scattering cell equipped with sapphire windows. (Figure 3.) For the block copolymer samples, thermal history is first erased by disordering the sample at ambient pressure prior to the experiments. Temperature control is provided via cartridge heaters inserted into an aluminum heating jacket and controlled using a PID controller. CO_2 is charged to the cell using a high-pressure manifold and manual syringe pump. The experiments were conducted at the National Institute of Standards and Technology, (NIST, Gaithersburg, MD) Cold Neutron Research Facility on the 30 m spectrometer. Instrument configuration was as follows, λ = 8 angstroms, $\Delta\lambda/\lambda$ = 15 %, sample diameter = 0.63 cm, sample to detector distance was 5 meters for the 32K copolymer sample and 6 meters for all others. 2-D raw data were normalized, corrected for background scattering and detector sensitivity, scaled to absolute differential scattering cross-sections (cm^{-1}) using SiO_2 standards and radially averaged to one dimension.
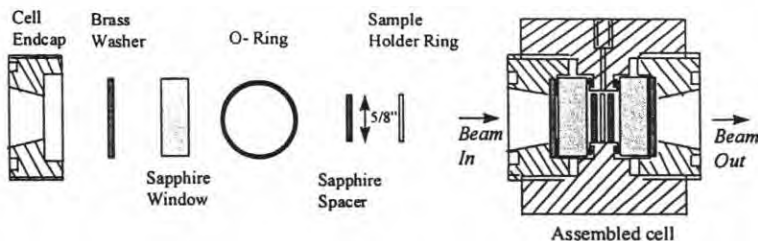

Figure 3. Schematic of the high-pressure neutron scattering cell.

4. Results and Discussion

The location of the LDOT for symmetric P(d-S-b-nBMA) copolymers having total molecular weights of 32,000 g/mol and 78,000 g/mol and the LCST for a 40% blend of d-PS and PnBMA homopolymers at ambient pressure are shown in Table 1. Our results are in agreement with literature reports.[15] The disparity between the LDOT for the 32K block copolymer and the LCST of homopolymer blends of d-PS and PnBMA chains having molecular weights nearly identical to the copolymer segments is a consequence of connectivity of the dissimilar blocks.

TABLE 1. Lower Critical Transitions in PS/PnBMA Block Copolymers and Blends

Symmetric Copolymers			40/60 d-PS/PnBMA Blend		
M_n	PDI	LCOT (°C)		M_n	PDI
32,000		Above T_d	d-PS	14,000	1.02
68,000	1.03	220	PnBMA	15,000	1.1
78,000	1.07	180			
			LCST = 126 °C		

We have studied the phase behavior of 78K P(d-S-b-nBMA) in the presence of CO_2 extensively. CO_2 sorption is known to be preferential for polyacrylates relative to polystyrene (Figure 2) and we conclude that in the dPS/PnBMA/CO_2 systems, PnBMA is selectively dilated. Figure 4 shows the SANS profile for the 78K sample as a function of density of the fluid phase at 145 °C. The data is presented in an IQ^2 vs. Q format to amplify second order reflections at twice the scattering vector of the primary peak that arise from a lamellar morphology, which is the expected ordered structure for this nearly symmetric copolymer. ($Q = 4\pi/\lambda \sin(\theta/2)$ is the scattering vector.) At ambient pressure, the broad and weak correlation peak indicates that the system is disordered. A second order reflection is not present. As density is increased (solid curves) above 0.05 g/cc (37 bar), there is a sharp increase in the maximum scattered intensity and a distinctive narrowing of the primary scattering peak that indicates the system has segregated and is now ordered. The emergence of a second order peak confirms that the LDOT has been crossed and the system is ordered. Reducing pressure (dashed curve) then causes the system to disorder. Therefore, despite a slight time-dependent hysteresis, SCF-induced LDOTs are fully reversible. At all temperatures between 60 and 180 °C we find the 78K copolymer is ordered at fluid densities above 0.1 g/cc.

The magnitude of CO_2-induced depressions in the LDOT is markedly evident in the behavior of the 32K copolymer. The disorder-order transition for this sample at ambient pressure is above the decomposition temperature (T_{dec}) of the copolymer and is thus inaccessible. In the presence of CO_2, however, the copolymer orders at 100 °C at fluid densities in excess of 0.3 g/cc (140 bar), more than 200 °C below the projected LDOT. The transition is accompanied by a discontinuous reduction in the half width of the first order peak as a function of density (Figure 5). In all cases, the degree of segregation increases with increasing pressure (density) and at all conditions exceeds that of systems ordered by thermal means at ambient pressure.
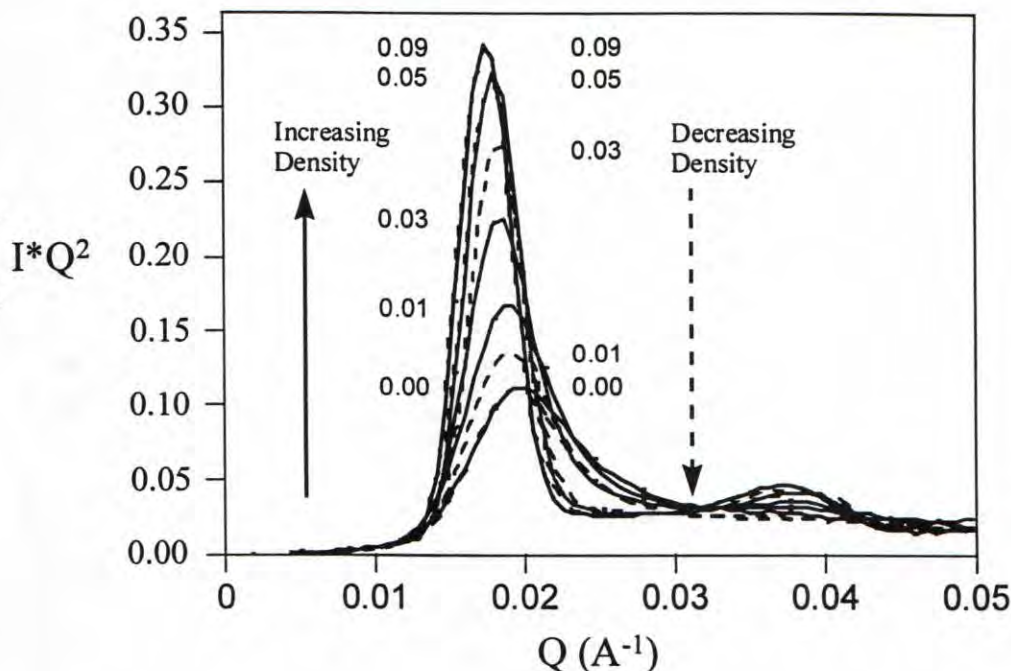
Figure 4. SANS profiles for a symmetric 78K P(d-S-b-nBMA) sample in the presence of CO_2 as a function of increasing (solid lines) and decreasing (dashed lines) CO_2 density at 145 ^{0}C. The CO_2 – induced transition is fully reversible.

The behavior of the P(d-S-b-nBMA) samples suggests that an analogous phase separation will be observed in low molecular weight blends of the copolymer components in the presence of CO_2. Figure 6a shows scattering profiles for a 40% d-PS and 60% PnBMA blend at 65 ^{0}C as a function of CO_2 density. Debye-Bueche analysis indicates that above a threshold density of 0.03 g/cc (18 bar), the correlation length begins to increase rapidly with increasing density (Figure 6b). Clearly, this system segregates at modest CO_2 densities at temperatures more than 60 ^{0}C below the ambient pressure LCST of 126 ^{0}C. The transition is fully reversible upon decompression.
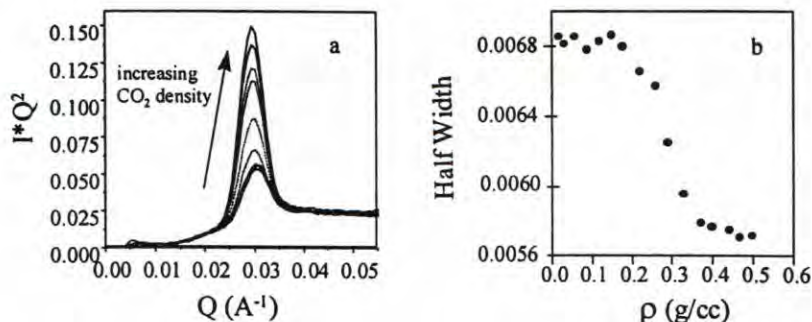
Figure 5. a.) SANS profiles for a symmetric 32K P(d-S-b-nBMA) sample in the presence of CO_2 as a function of increasing CO_2 density at 100 °C. b.) Half-width of the primary scattering peak plotted as a function of CO_2 density. The discontinuity at approximately 0.3 g/cc indicates a transition from the disordered to ordered state.
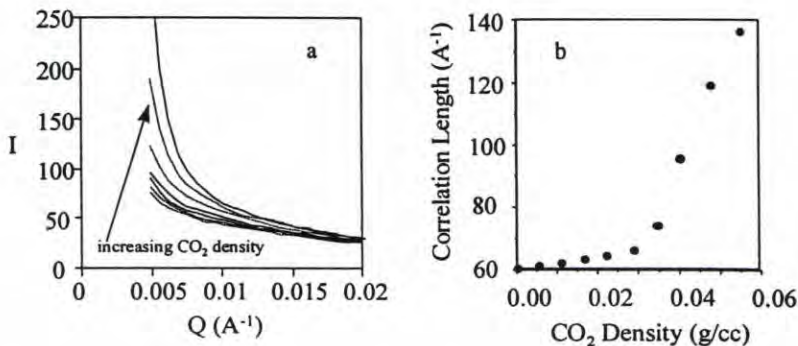

Figure 6. a.) SANS profile of a PS/PnBMA blend as a function of increasing CO_2 density at 65 °C. b.) Correlation lengths calculated from SANS data as a function of increasing CO_2 density at 65 °C. The rapid increase in the length scale of the concentration fluctuation at approximately 0.03 g/cc reveals a transition from the phase-mixed to the phase separated state.

Figure 2b indicates that CO_2 sorption is preferential for PVME relative to PS. In homogeneous d-PS/PVME blends this disparity leads to phase separation upon exposure to SCF CO_2. At ambient pressure, a 50/50 blend of d-PS and PVME showed a rapid increase in scattered intensity with increasing temperature indicating the approach to the LCST from the homogeneous state. (Figure 7a.) Analysis of the data yields a transition temperature of 155 °C. Figure 7b. shows the scattered intensity for the blend at 40 °C as a function of the density of compressed carbon dioxide in contact with the blend. At ambient pressure the blend is clearly phase-mixed, however at a slightly elevated CO_2 pressure (24 bar) sorption of CO_2 induces phase separation as indicated by divergence of the scattered intensity at low Q. Note that this dramatic reduction in the LCST, 115 °C, occurs at a CO_2 uptake of less than 3.5% (see figure 2).
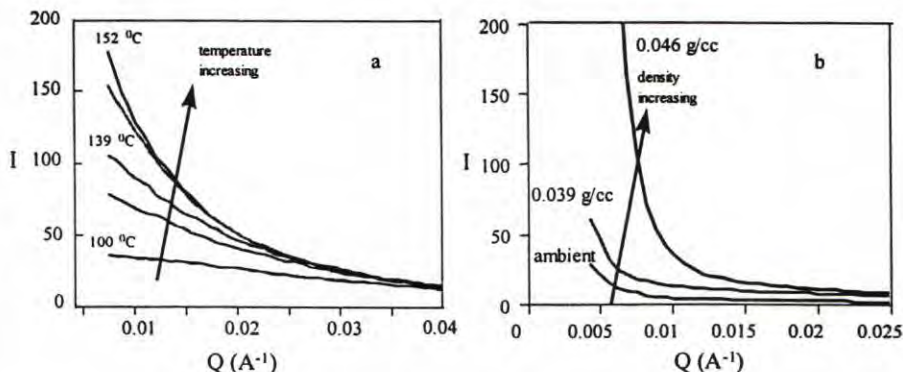
Figure 7. a.) SANS profile of a PS/PVME blend as a function of temperature at ambient pressure. The divergence of scattered intensity at low Q reveals an LCST of 155 °C b.) SANS profile of a PS/PVME blend as a function of density at 40 °C. Again, the divergence of scattered intensity at low Q reveals transition from the phase-mixed to the phase separated state.

4.1 THE NATURE OF CO_2 – INDUCED DEPRESSIONS IN LOWER CRITICAL TRANSITIONS

At first glance, one might consider the effect of compressed CO_2 on the phase behavior of multi-component polymer systems to be a simple combination of the known effects of liquid solvents and hydrostatic pressure. Solvent effects are primarily enthapic in nature and typically manifest in upper critical solution behavior. Common solvents mitigate unfavorable interactions between dissimilar segments and enhance miscibility. In blends, the addition of highly selective solvents, e.g. a non-solvent for one component, can lead to precipitation of the unfavored species at high dilution.[34] In block copolymers, the effect of selective solvents is less clear, but studies to date reveal a collection of the solvent at the domain interface, selective dilation of one phase, and stabilization of the disordered phase via depression of the UODT.[35] The systems we have studied each exhibit a lower critical transition. For these specific systems, previous work indicates the hydrostatic pressure suppresses free volume differences between the components and expands the region of miscibility.[19,25]

Blends of d-PS and PVME exhibit a weakly attractive charge transfer interaction between the segments. In the d-PS/PnBMA systems, exothermic intersegment-interactions do not exist.[36] Thus entropic contibutions to lower critical transitions are important in both systems, and clearly dominant in the latter. We find that for the d-PS/PVME and d-PS/PnBMA systems sorption of ~3% of CO_2 can induce phase separation at temperatures 100s of degrees below the ambient pressure transition. The origin of this behavior can be identified by examining the influence of CO_2 sorption on free-volume differences between the polymeric components, which in the absence of strong specific interactions, drive lower critical phase transitions.

Application of stability criteria to the ternary system via differentiation of Gibbs free energy reveals that compressibility plays a central role. Specifically, the system is destabilized as compressibility increases. Compressibility can in turn be calculated using an appropriate equation of state. We choose the Sanchez-Lacombe EOS[37,39] which can be written

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] = 0 \tag{1}$$

where $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ are reduced pressure, temperature and density and r represents the number of lattice sites occupied by the molecule. For mixtures we employ mixing rules prescribed by Sanchez[37] that include an adjustable interaction parameter to account for mixture non-ideality. The S-L EOS is shown in figure 2 to faithfully reproduce CO_2 sorption curves in PS, PVME and PS/PVME blends. The pure component parameters are literature values.[5,37,39] The binary interaction parameters used in models are indicated in caption of figure 2. The PS/PVME/CO_2 system was modeled as a pseudo-binary using characteristic parameters for the blend calculated using the pure component parameters and a PS/PVME interaction parameter obtained by fitting the composition dependence of the binary PS/PVME LCST.[40]

The determination of the interaction parameter for the polymer/CO2 mixture leads directly to the determination of specific volumes of the mixture at any inclusive condition. Compressibilities for such systems are difficult to measure experimentally, but calculations using the EOS are straightforward. At a given condition, we calculate the volume of the mixture as a function of hydrostatic pressure at constant composition. Compliant with its definition, compressibility is then obtained through the numerical differentiation via:

$$\beta = \frac{-1}{v}\left[\frac{dv}{dP}\right]_{T,w} \tag{2}$$

Here, w is the mixture composition. The results indicate that the compressibility of the mixture increases with increase in CO_2 pressure. This occurs for two reasons: a) CO_2 is a high free volume diluent that increases compressibility of the mixture relative to that of the pure polymer and b) CO_2 sorption in the mixture increases with pressure. We did not calculate the compressibility of the PS/CO_2 binary as PS is below the glass transition temperature at these conditions although it is expected to be quite small. Also shown in the figure is the compressibility of a PS/PVME blend under the influence of hydrostatic pressure only calculated using the Sanchez-Balasz modification to the SL-EOS.[38]
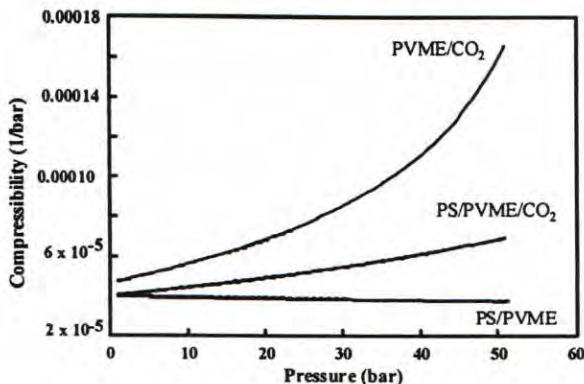
Figure 8. Compressibility of PVME/CO$_2$, PS-PVME 50-50 blend/CO$_2$, and PS/PVME mixtures at 20 ^{0}C calculated using the Sanchez-Lacombe equation of state.

The trends depicted in figure 8 shed light on the nature of the CO$_2$-induced transitions. Compressibility of the phase-mixed system increases rapidly with CO$_2$ sorption and differential dilation of the components leads to a disparate increase in compressibility of the segregated components. This free-volume disparity imposes a large negative volume change on mixing that ultimately results in phase separation. As expected, in the absence of diluent, compressibility decreases with pressure. This result is consistent with the increase in the LCST of PS/PVME blends with hydrostatic pressure.[25]

While the influence of CO$_2$ sorption on the systems studied here results in phase segregation by a depression of the lower critical transition, the results do not exclude the probability that for some systems CO$_2$ sorption at high pressure (or low temperature) will promote miscibility near the UODT or UCST where the transition is dominated by enthalpic considerations. At liquid-like densities, its influence could mimic that of common liquid solvents by mitigating unfavorable contacts. Indeed this is the case for block copolymers of polyisoprene and polystyrene.[41]

5. Conclusions

We have shown that sorption of a few weight percent of carbon dioxide in polymer blends and block copolymers can depress the location of lower critical solution transitions by hundreds of degrees. These solvent-induced transitions can occur at CO$_2$ vapor densities of less than 0.05 g/cc. The sensitivity of the transitions to minor dilation with CO$_2$ and the results of the compressibility calculations presented here suggest the effect is entropic rather than enthalpic in nature.

288

Acknowledgments

References

1. McHugh, M. A.; Krukonis, V. J. (1986) *Supercritical Fluid Extraction: Principles and Practice*; Butterworths: Boston.
2. DeSimone, J. M.; Maury, E.E.; Menceloglu, Y.Z.; McClain, J.B.; Romack, T.J.; Combes, J.R. (1994) Dispersion Polymerizations in Supercritical Carbon Dioxide, *Science* 265, 356-359.
3. Gross, S. M.; Givens, R. D.; Jikei, M.; Royer, J. R.; Khan, S.; DeSimine, J. M.; Odell, P. G.; Hamer, G. K. (1998) Synthesis and Swelling of Poly(bisphenol A carbonate) Using Supercritical CO_2, *Macromolecules*, 31, 9090-9092.
4. Watkins, J. J. and McCarthy, T. J. (1995) Polymerization of Styrene in Supercritical CO_2-Swollen Poly(Chlorotrifluoroethylene), *Macromolecules* 28, 4067-4074. Watkins, J. J. and McCarthy, T. J. (1995) Polymer/Metal Nanocomposite Synthesis in Supercritical CO_2, *Chem. Mater.*, 7, 1991-1994.
5. Kiszka, M. B.; Meilchen, M. A,; McHugh, M. A. (1988) Modeling High-Pressure Gas-Polymer Mixtures Using the Sanchez-Lacombe Equation of State, *J. Appl. Polym. Sci.* 36, 583-587.
6. Garg, A.; Gulari, E.; Manke, C. W. (1994) Thermodynamics of Polymer Melts Swollen with Supercritical Fluids, *Macromolecules* 27, 5643-5653.
7. Condo, P. D.; Johnston, K. P. (1994) In Situ Measurement of the Glass Transition Temperature of Polymers with Compressed Fluid Diluents, *J Polym. Sci. Polym. Phys.* 32, 523-533.
8. Lecture presented at the NATO ASI on Supercritcal Fluids, Kemer, Turkey, 1998
9. Chapman, B. R.; Gochanour, C. R.; Paulaitis, M. E. (1996) CO_2 -Enhanced Diffusion ofAzobenzene in Glassy Polystyrene near the Glass Transition, *Macromolecules*, 29, 5635 - 5649.
10. Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. (1992) Application of Compressed Carbon Dioxide in the Incorporation of Additives into Polymers, *J. Appl. Polym. Sci.* 46, 231.
11. Watkins, J. J.; Brown. G. D.; RamachandraRao, V. S.; Pollard, M. A. Russell (1999) Phase Separation in Multi-Component Polymer Systems Induced by Compressible Solvents, submitted to *Macromolecules*.
12. Flory, P. J. (1970) Thermodynamics of Polymer Solutions, *Discuss. Faraday. Soc.*, 49, 7- 29.
13. De Gennes, P.-G. (1979) Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY.
14. Sanchez, I. C. (1987) Polymer Phase Separation, in *Encyclopedia of Physical Science and Technology*; Academic Press: New York, Vol. XI 1-18.
15. Russell, T. P.; Karis, T. E.; Gallot, Y.; Mayes, A. M. (1994) A Lower Critical Ordering Transition in a Diblock Copolymer Melt, *Nature* 368, 729-731.
16. Balsara, N. P.; Perahia, D.; Safinya, C. R.; Tirrell, M.; Lodge, T. P. (1992) Birefringence Detection of the Order-to-Disorder Transition in Block Copolymer Liquids, *Macromolecules* 25, 3896-3901.
17. Lodge, T.P.; Pan, C.; Jin, X.; Liu, Z.; Zhao, J.; Maurer, W. W.; Bates, F. S. (1995) Failure of the Dilution Approximation in Block Copolymer Solutions, *J. Polym. Sci. Polym. Phys.* 33, 2289-2293.
18. Tanaka, H.; Hashimoto, T. (1991) Thermal Concentration Fluctuations of Block Polymer/Homopolymer Mixtures in the Disordered State. 1.Binary Mixtures of SI/HS, *Macromolecules* 24, 5398-5407.
19. Pollard, M.; Russell, T. P.; Ruzette, A. V.; Mayes, A. M.; Gallot, Y. (1998) The Effect of Hydrostatic Pressure on the Lower Critical Ordering Transition in Diblock Copolymers, *Macromolecules*, in press.
20. Janssen, S.; Schwahn, D.; Mortensen, K.; Springer, T. (1993) Pressure Dependence of the Flory-Huggins Interaction Parameter in Polymer Blends: A SANS study and a comparison to the Flory-Orwoll-Vrij Equation of State, *Macromolecules*, 26, 5587-5591.
21. Hammouda, B.; Bauer, B. J. (1995) Compressibility of Two Polymer Blend Mixtures, *Macromolecules* 28, 4505-4508.
22. Hajduk, D. A.; Gruner, S. M.; Erramilli, S.; Register, R. A.; Fetters, L. J. (1996) High-Pressure Effects on the Order-Disorder Transition in Block Copolymer Melts, *Macromolecules*, 29, 1473-1481.

23. Schwahn, D; Frielinghaus, H.; Mortensen, K.; Almdal, K. (1996) Temperature and Pressure Dependence of the Order Parameter Fluctuations, Conformational Compressibility, and the Phase Diagram of the PEP-PDMS Diblock Copolymer, *Phys. Rev. Lett.* 77, 3153 – 3156.

24. Steinhoff, B.; Rullmann, M.; Wenzel, M.; Junker, M.; Alig, I.; Oser, R.; Stuhn, B.; Meier, G.; Diat, O.; Bosecke, P.; Stanley, H. B. (1998) Pressure Dependence of the Order-to-Disorder Transition in Polystyrene/Polyisoprene and Polystyrene/Poly(methylphenylsiloxane) Diblock Copolymers, *Macromolecules*, **31**, 36-40.

25. An, L.; Horst, R.; Wolf, B. A.; (1997) Pressure Dependence of the Miscibility of Poly(vinyl methyl ether) and Polystyrene: Theoretical Representation, *J. Chem. Phys.*, **107**, 2597-2602.

26. McHugh, M. A.; Guckes, T. L. (1985) Separating Polymer Solutions with Supercritical Fluids, *Macromolecules*, **18**, 674-680.

27. McClellan, A. K.; Bauman, E. G.; McHugh, M. A. (1985) Polymer Solution-Supercritical Fluid Phase Behavior in *Supercritical Fluid Technology*, Penninger, J. M. L.; Radosz, M.; McHugh, M. A.; Krukonis, V. J. eds.; Elsevier Science Publishers B. V., Amsterdam, Netherlands.

28. Kiran, E.; Xiong, Y,; Zhuang, W. (1993) Modelling Polyethylene Solutions in Near and Supercritical Fluid Solutions Using the Sanchez-Lacombe Model, *J. Supercrit. Fluids*, 6, 193-203.

29. McHugh, M. A.; Krukonis, V. J. (1989) Supercritical Fluids, in *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. eds.; John Wiley & Sons: New York, vol. 16.

30. Masson, J. C. (1989) in *Polymer Handbook, 3rd. ed;* Brandrup, J.; Immergut, E. H. Eds.; John Wiley and Sons: New York, p.II/1.

31. Wang, N.-H.; Takishima, S.; Masuoka, H. (1994) Measurement and Correlation of Solubility of a High Pressure Gas in a Polymer by Piezoelectric Quartz Sorption - CO_2 + PVAC and CO_2 + PBME Systems, *Int. Chemical Eng.*, 34, 255-262.

32. Wissinger, R. G.; Paulaitis, M. E. (1987) Swelling and Sorption in Polymer-CO_2 Mixtures at Elevated Pressures, *J. Polym. Sci. Polym. Phys.*, 25, 2497- 2510.

33. Mokdad, A.; Dubault, A.; Monnerie, L. (1996) Sorption and Diffusion of Carbon Dioxide in Single-Phase Polystyrene/Poly(vinylmethylether) Blends, *J. Polym. Sci. Polym. Phys.*, 34, 2723-2730.

34. Robard, A.; Patterson, D. (1977) Temperature Dependence of Polystyrene - Poly(vinyl methyl ether) Compatibility in Trichloroethene, *Macromolecules*, 10, 1021-1025.

35. Lodge, T. P.; Hamersky, M. W.; Hanley, K. J.; Huang, C.-I (1997) Solvent Distribution in Weakly-ordered Block Copolymer Solutions, *Macromolecules*, 30, 6139-6149.

36. Ruzette, A.-V. G.; Banerjee, P.; Mayes, A. M.; Pollard, M.; Russell, T.P.; Jerome, R.; Slawecki, T.; Hjelm, R.; Thiyagarajan, P. (1998) Phase Behavior of Diblock Copolymers between Styrene and n-Alkyl Methacrylates *Macromolecules*, 31, 8509-8516.

37. Sanchez, I. C.; Lacombe, R. H. (1978) Statistical Mechanics of Polymer Solutions, *Macromolecules* 11, 1145 – 1156.

38. Sanchez, I. C.; Balasz, A. C. (1989) Generalization of the Lattice-Fluid Model for Specific Interactions, *Macromolecules*, 22, 2325-2331.

39. Sanchez, I. C.; Lacombe, R. H. (1977) An Elementary Equation of State for Polymer Liquids, *J. Polym. Sci. Polym. Lett.* 15, 71-75.

40. Halary, J. L.; Ubrich, J. M.; Nunzi, J. M.; Monnerie, L.; Stein, R. S. (1984) Phase Separation in Polystyrene-Poly(vinylmethylether) Blends: A Fluorescence Emission Analysis, *Polymer*, 25, 956 – 962.

41. Vogt, B.D.; Brown, G. D.; RamachandraRao, V. S.; Watkins, J. J. (1999) submitted to *Macromolecules*.